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MEMORANDUM FOR PRS (~~Contractor~~/In-House Publication)

FROM: PROI (TI) (STINFO) 24 June 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0159
S. Tam and M.E. Fajardo, "Quantitative Matrix Isolation Spectroscopy in Heavily Doped Millimeters Thick Parahydrogen Solids"

Gordon Research Conference (International) **(Statement A)**

GORDON CONFERENCE, PHYSICS AND CHEMISTRY OF MATRIX ISOLATED SPECIES
PLYMOUTH, NH, 11-15 JULY 1999

Quantitative Matrix Isolation Spectroscopy in Heavily Doped Millimeters Thick Parahydrogen Solids

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OLD
Slide

TASK OBJECTIVE

Develop a technique for quantifying dopant species identities and concentrations in optically dense samples using the dopant-induced infrared (IR) absorptions.

BACKGROUND

Have demonstrated we can produce gram scale samples of solid pH_2 doped with HEDM species with concentrations of 0.01 to 0.1%.

Dopants were produced using laser ablation which is not a suitable method for producing high concentrations.

Three teams in the Cryosolids Working Group tasked with: 1) developing new dopant sources; 2) developing a diagnostic for characterizing the new sources; and **3) developing diagnostic tools for detecting the products of these new sources in pH_2.**

APPROACH

Direct absorption measurements of thick, heavily concentrated samples of HEDM doped pH_2 solids will not work as a diagnostic for these new sources.

Alternative is to use the dopant-induced IR absorptions as a diagnostic.

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High Energy Density Matter (HEDM) Cryosolid Propellants

HEDM Cryosolid Program Objectives

Trap 5% molar concentration of energetic additives in solid hydrogen.
Demonstrate size-scaleable sample production method.

Payoffs

Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

LOX/LH_2: $I_{sp} = 390$ s
5% B/H_2 + LOX: $I_{sp} = 500$ s (+30%)*

*calculated for $P_{chamber} = 1000$ psia, $P_{exhaust} = 14.7$ psia

Greater Propellant Density

liquid H_2 : $= 0.070$ g/cm^3
solid H_2 : $= 0.087$ g/cm^3 (+25%)
50/50 liquid He/solid H_2 : $= 0.105$ g/cm^3 (+50%)

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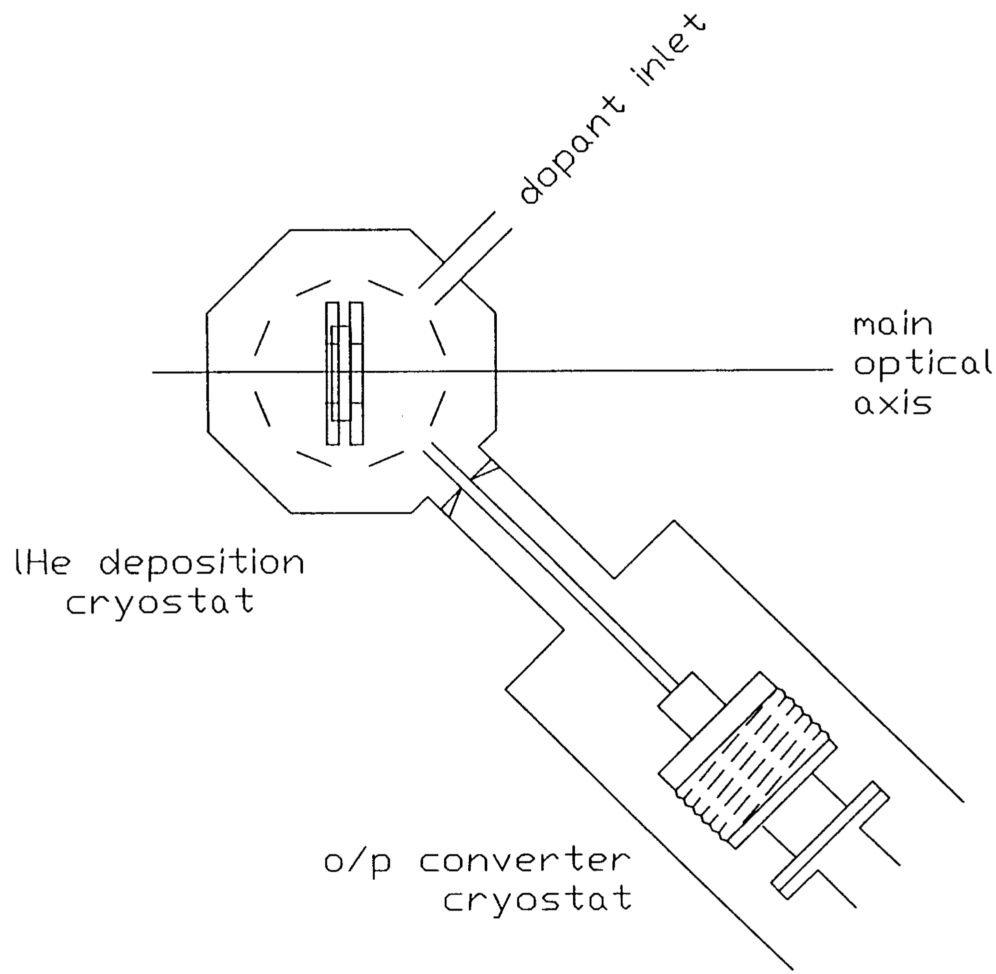
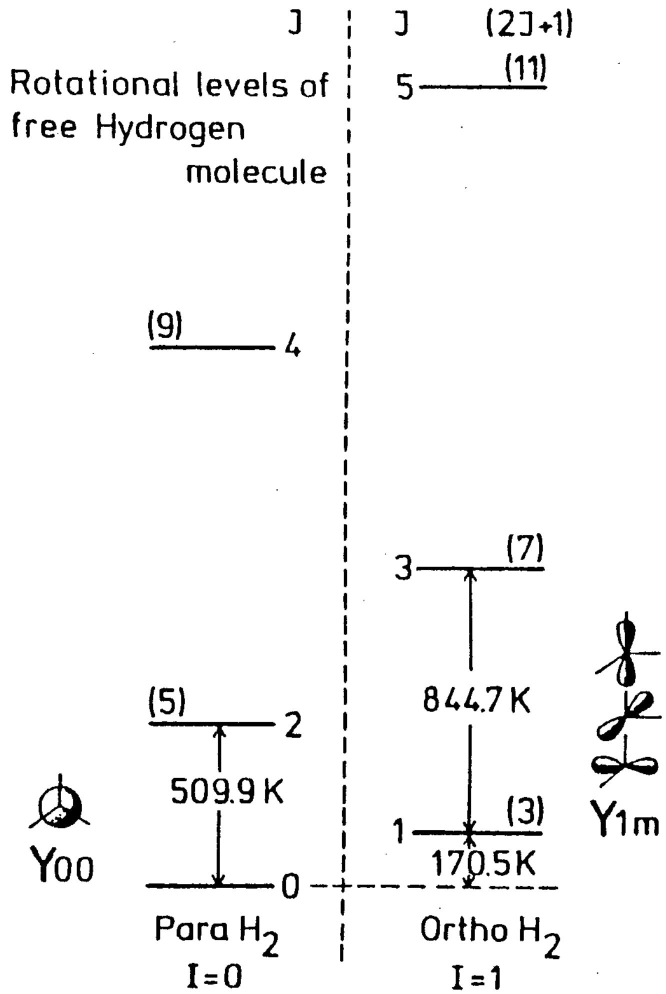
Experimental Diagram



NEW

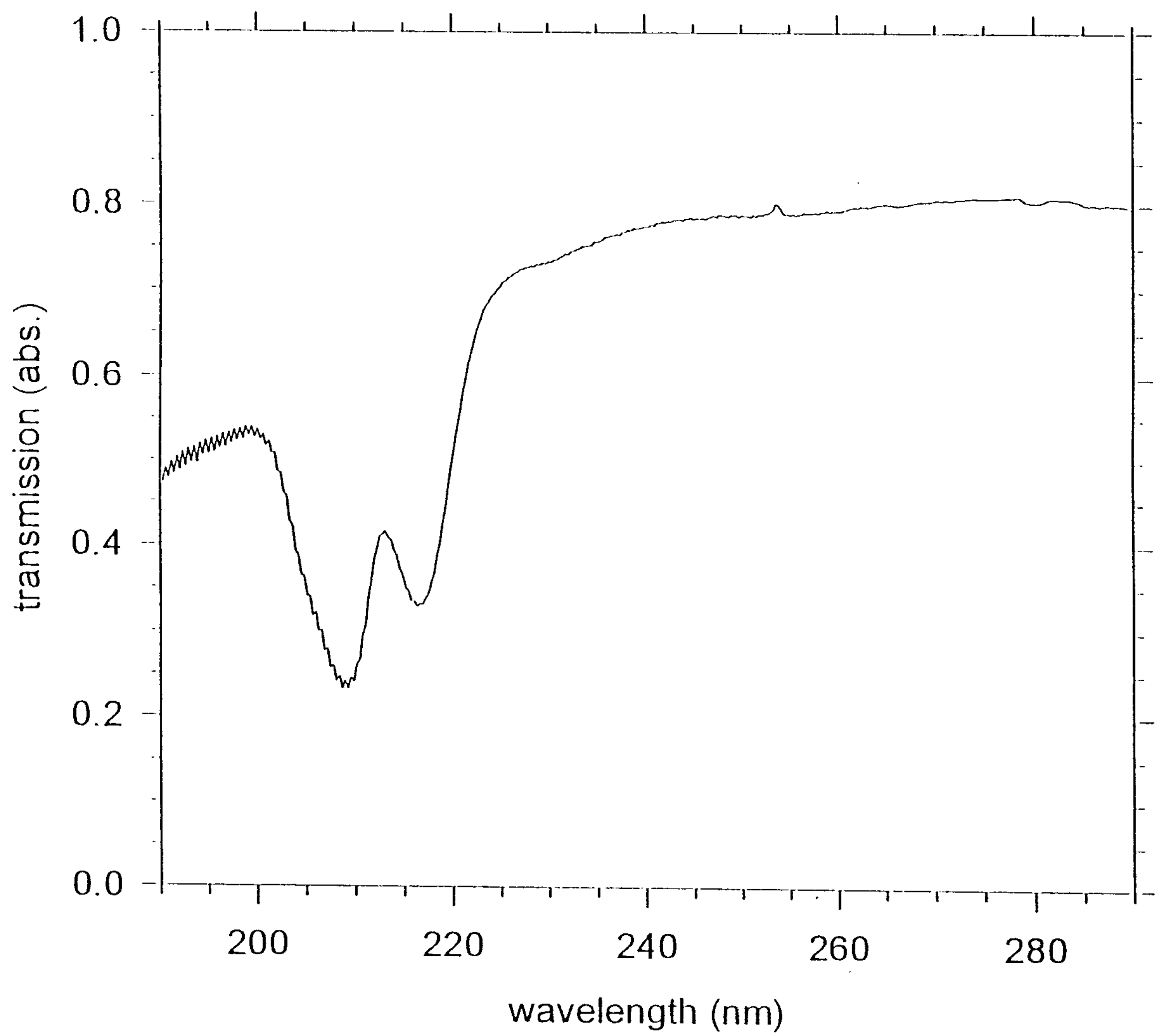
Ortho- and Para-Hydrogen



I.F. Silvera
Rev. Mod. Phys.,
52, 393 (1980).

Nas ~~Ehh~~ 5/21/02

B Ablation in p-H_2 Matrix Transmission Spectrum at 2 K

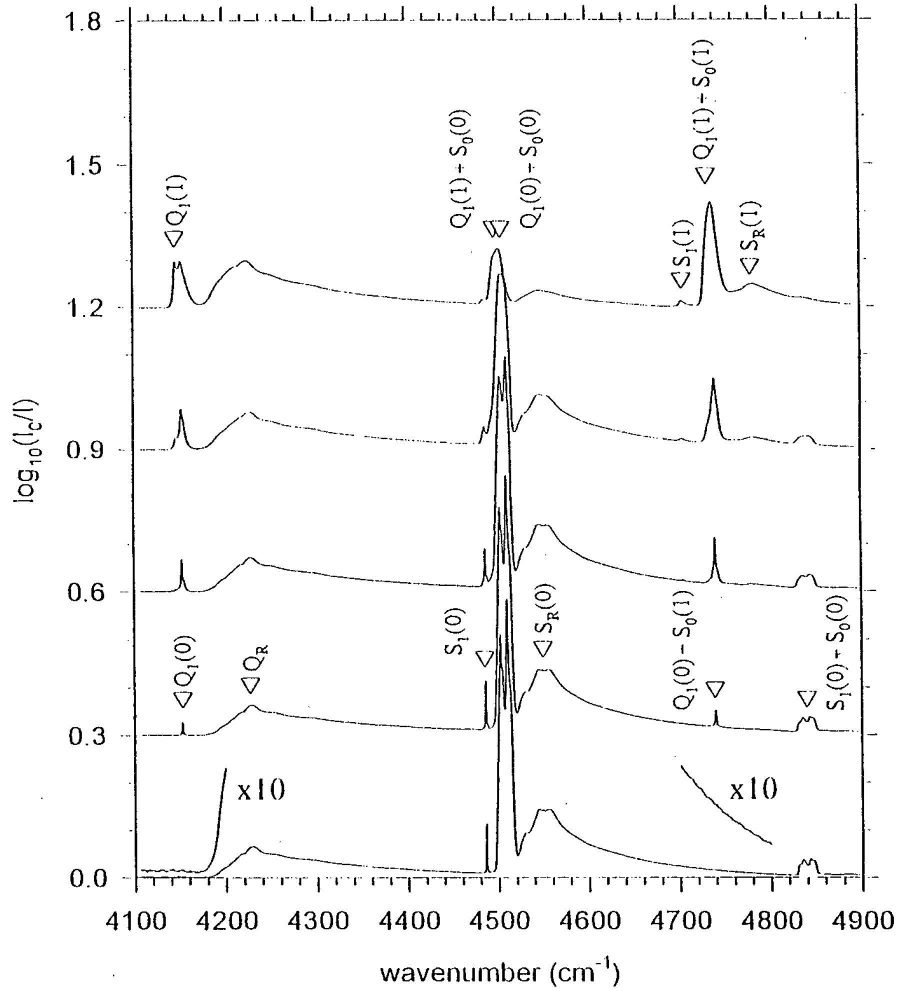


NOTE:
Transmission = 0.8
at 240 nm!

NEW

Demonstration of Control of o-H_2 Fraction

At 0% o-H2:
Observation of $S_1(0)$ and non-observation of $Q_1(0)$ implies h.c.p. solid

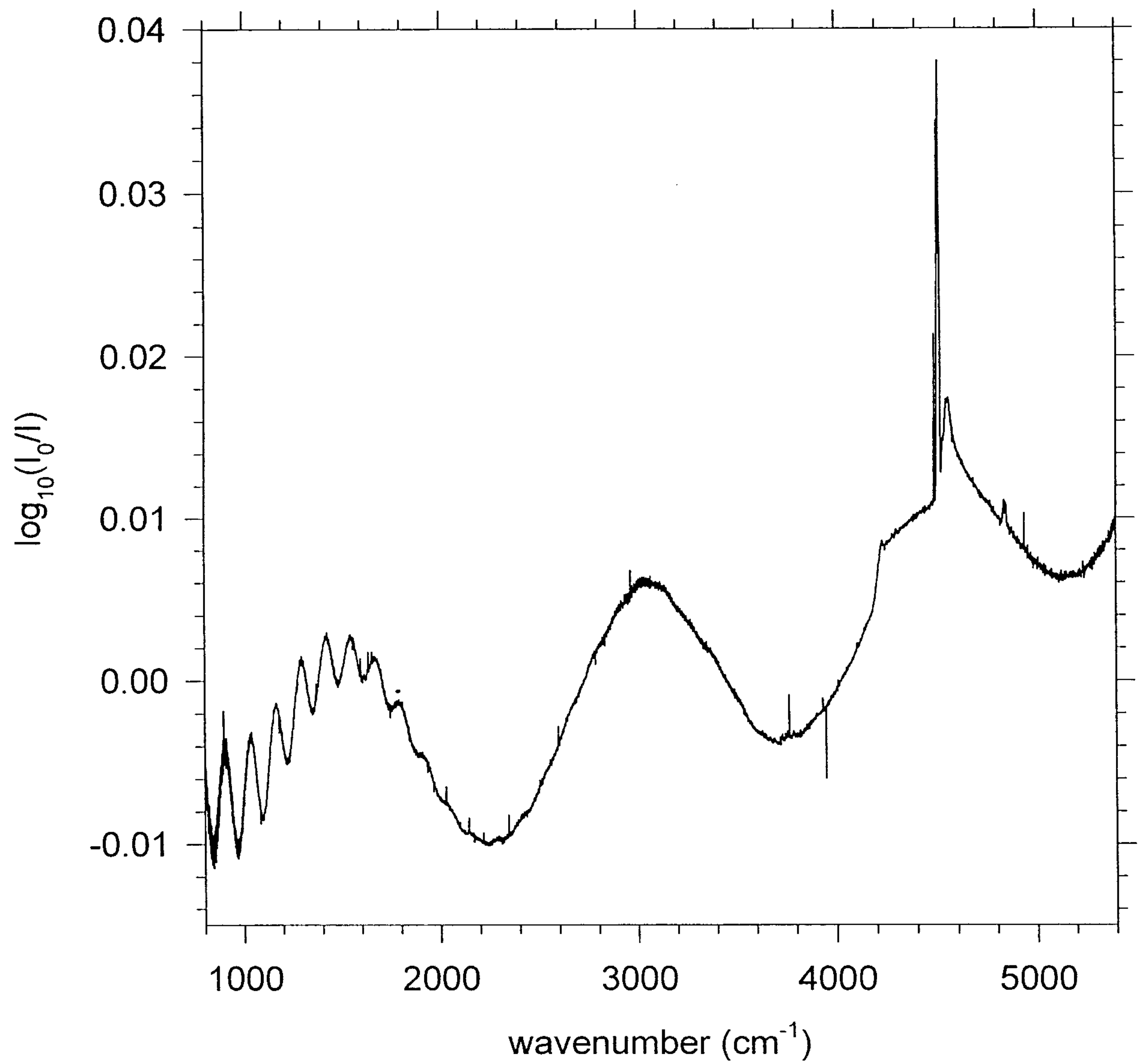


Convertor Temp	% o-H_2
135 K	70
52 K	25
37 K	8
28 K	2
15 K	< 0.01

Reference:
J. van Kranendonk & H.P. Gush, Phys. Lett., **1**, 22 (1962).

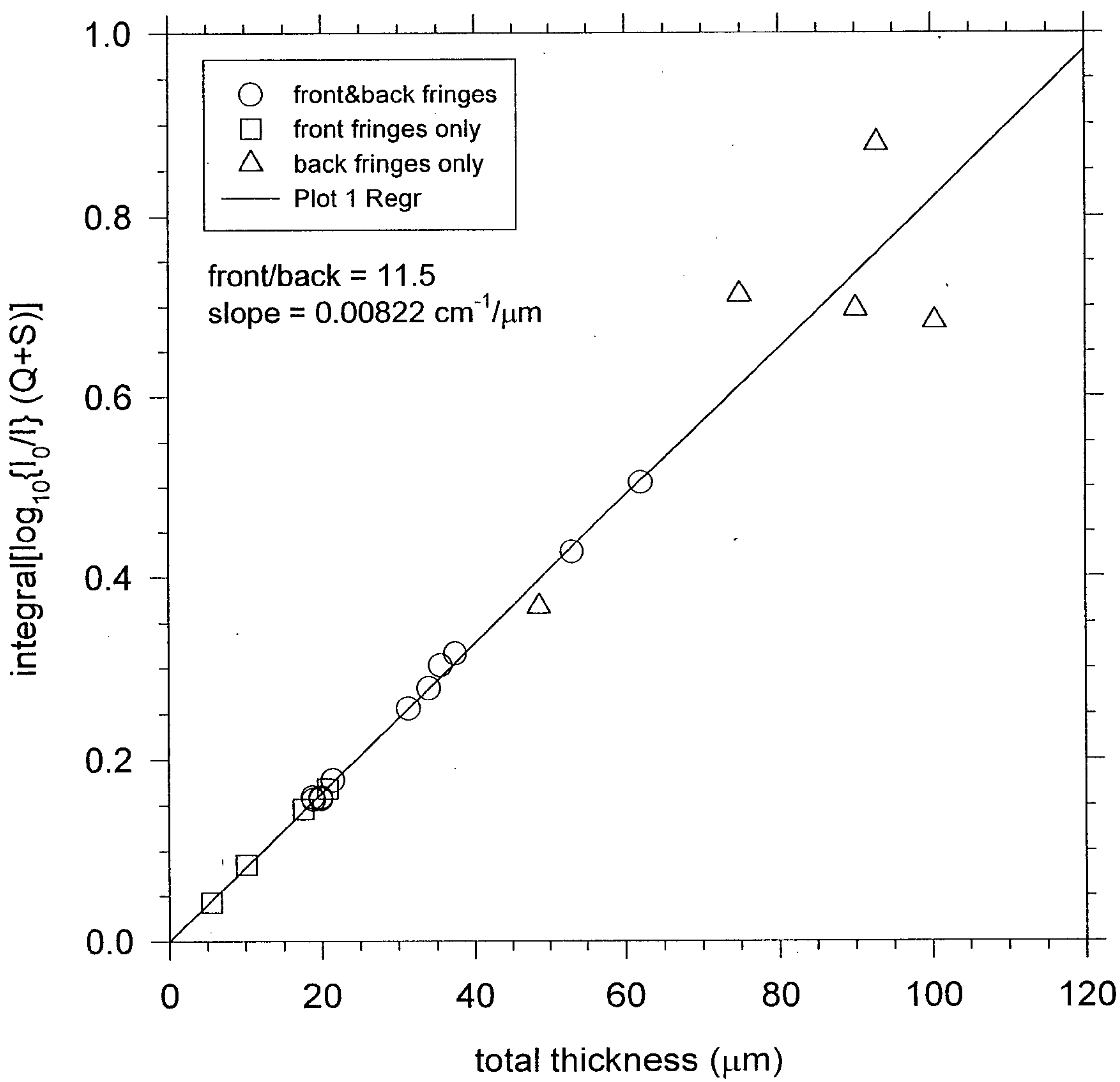
NEW

IR Absorption Spectrum of a 37.4 μm Thick Vapor Deposited pH_2 Solid (34.4 μm front + 3.0 μm back)



NEW

Correlation of the Total Thickness Determined by Interferometry versus the Integrated Absorption Intensity of the $Q_1(0)+S_0(0)$ Transition of Solid pH_2



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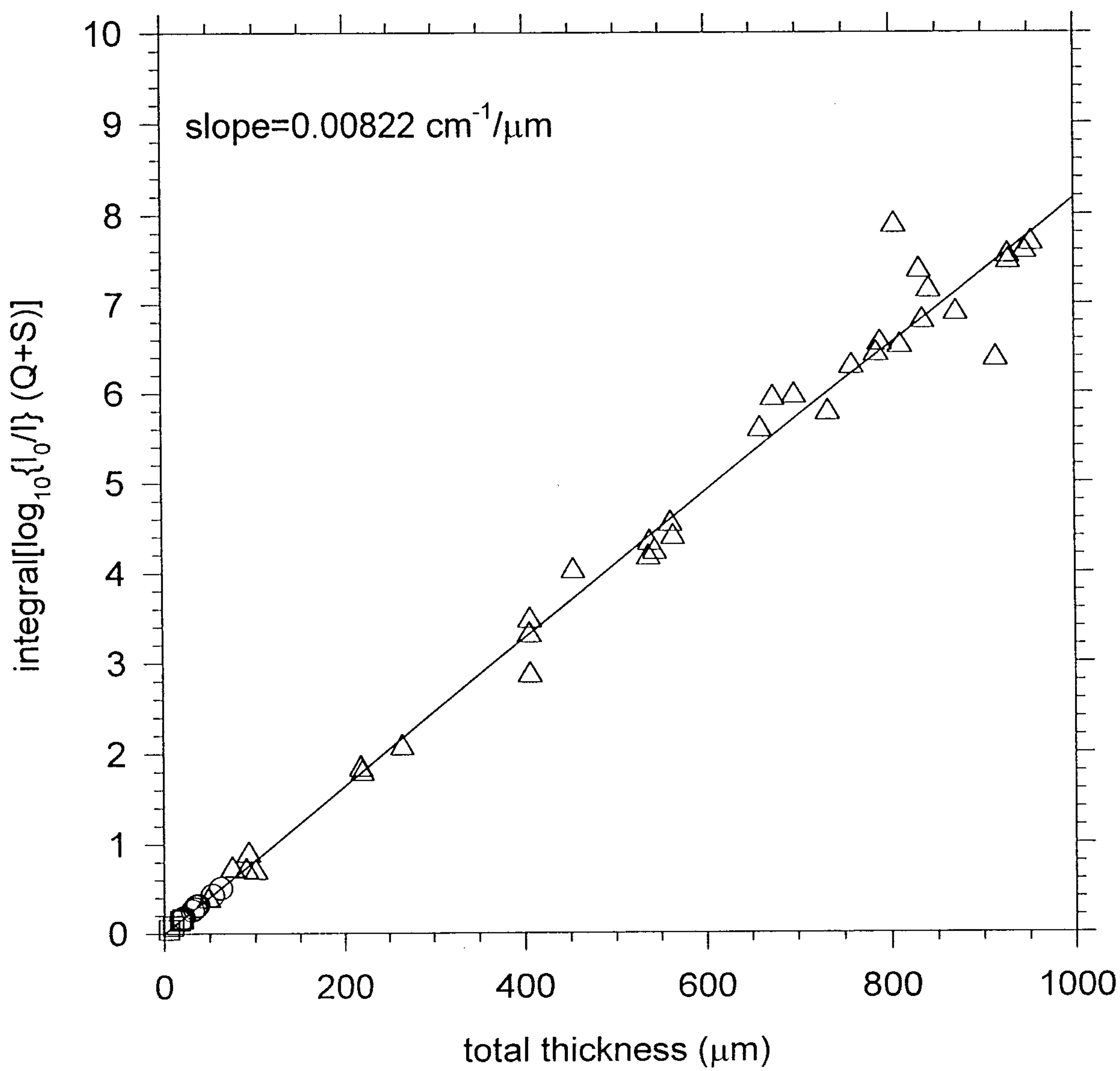
Extraplation of the Total Thickness versus the Integrated Absorption Intensity of the $Q_1(0)+S_0(0)$ Transition of Solid pH_2



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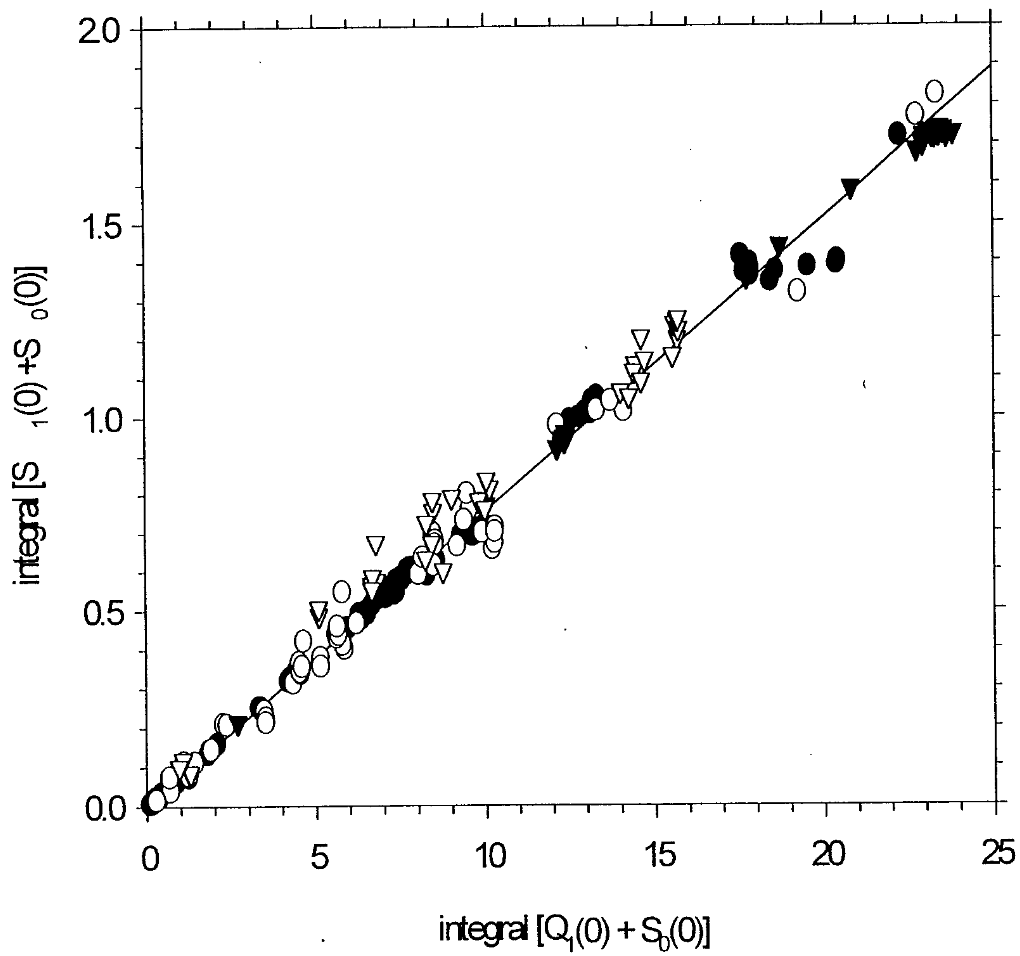
Correlation between the Integrated Intensities of the $Q_1(0)+S_0(0)$ and $S_1(0)+S_0(0)$ Transitions of Vapor Deposited pH_2 Solids



NOTES

$\alpha_{Q+S} = 188\ \mathrm{cm}^{-2}$

$\alpha_{S+S} = 0.0757\ \alpha_{Q+S} = 14.2\ \mathrm{cm}^{-2}$

For determining thickness:

Band	**Range**
$Q_1(0)+S_0(0)$	0-1 mm
$S_1(0)+S_0(0)$	1-10 mm

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Beer's Law

$$A(\tilde{\nu}) \equiv 2.303 \quad \log_{10}(\frac{I_0}{I}) = \alpha c l$$

$$c = \frac{A(\tilde{\nu})}{\alpha\, l} \Rightarrow \frac{2.303 \int_{band} \log_{10}(\frac{I_0}{I}) d\tilde{\nu}}{l \int_{band} \alpha(\tilde{\nu}) d\tilde{\nu}}$$

Increased path lengths or highly concentrated samples can cause saturation of the absorption.

If we want to work with gram scale, heavily-doped pH_2 samples, we require a spectral feature that has a very small intrinsic absorption coefficient (α) to compensate for the higher c and l.

We can use dopant-induced infrared absorptions to determine the concentration.

BUT: Need to determine $\alpha_{ind} \equiv$ the dopant-host intrinsic absorption strength

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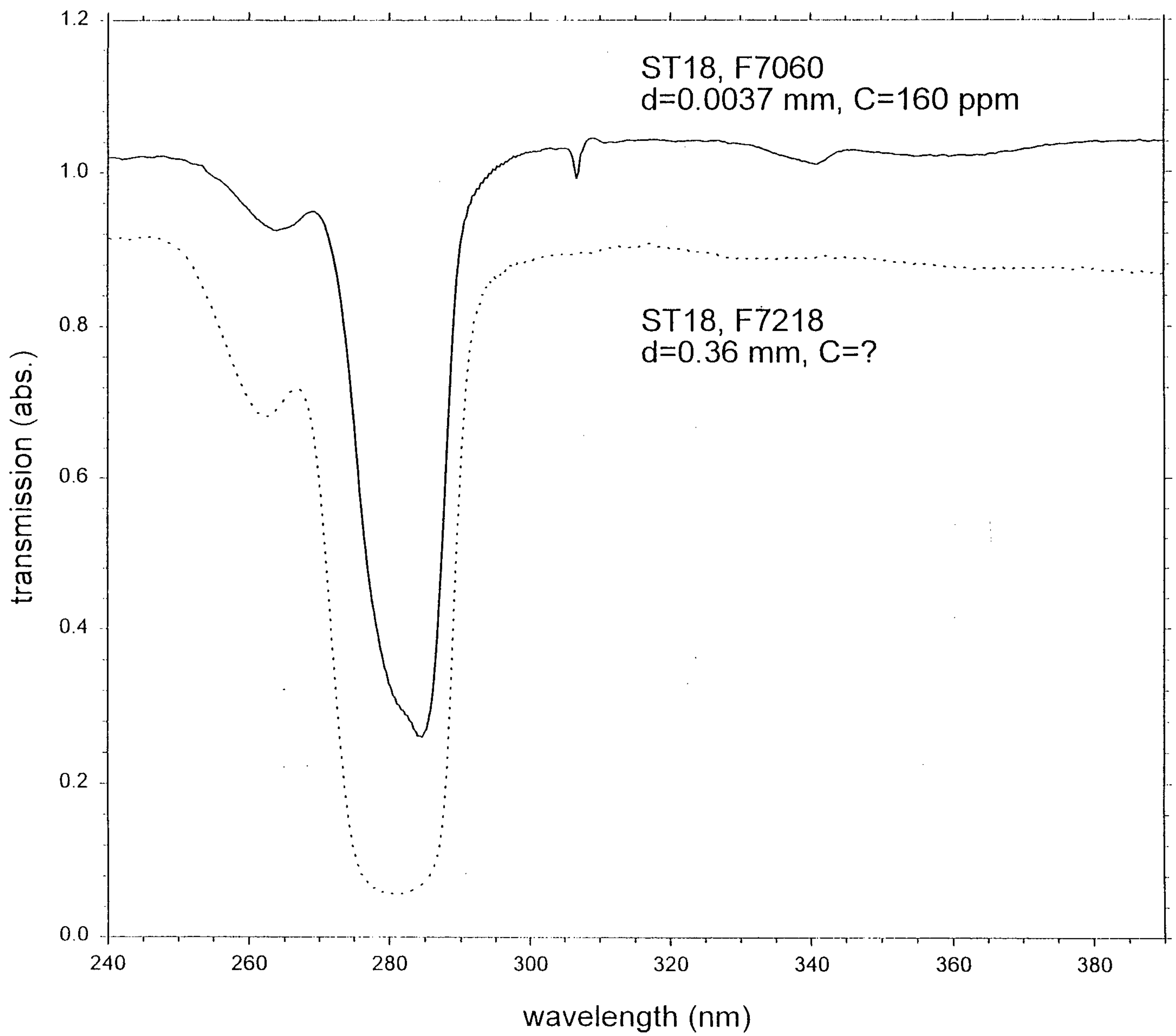
Mg/pH_2 and Mg/oD_2, T=2 K



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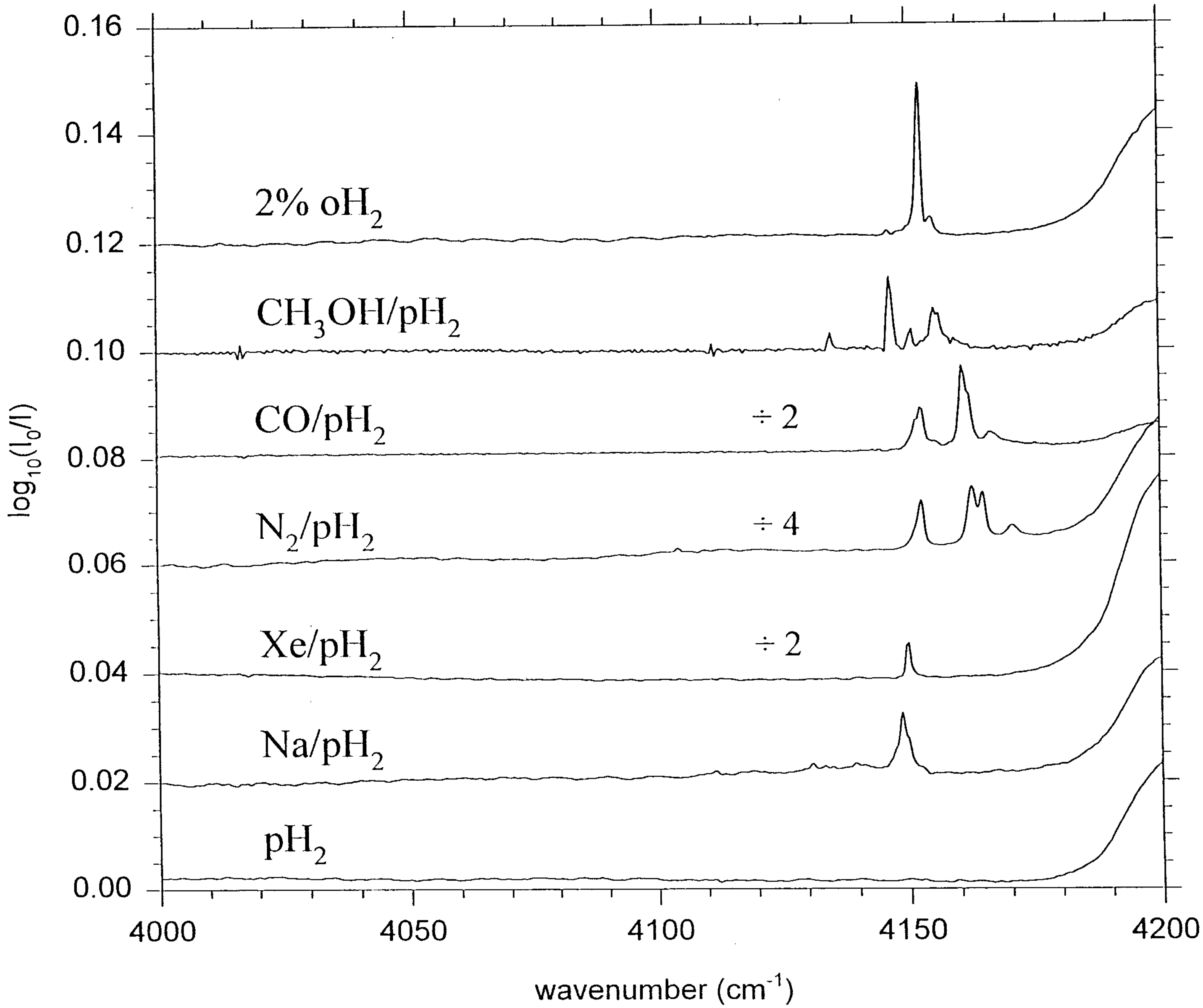
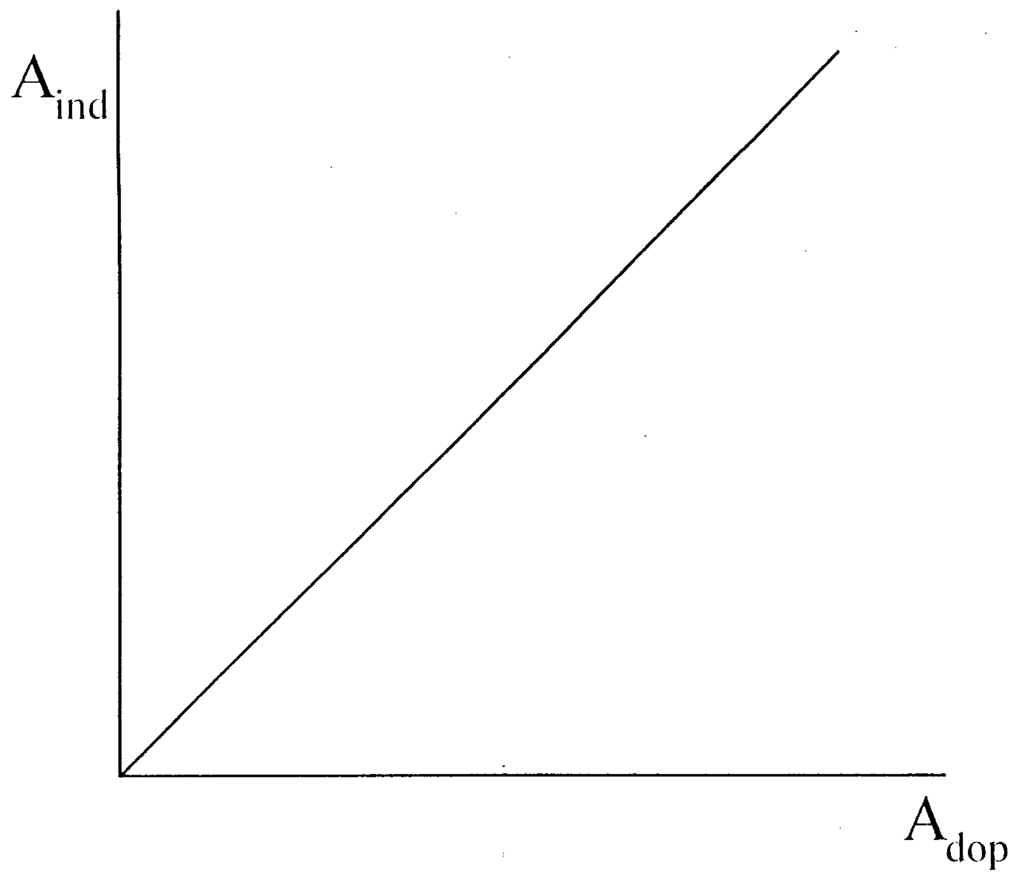
Examples of Dopant Induced H_2 Absorptions



Determining α_{ind} from α



Where:

Slope of the line $= \dfrac{\alpha_{ind}}{\alpha}$

$\alpha \equiv$ property of the dopant in the gas phase

$\alpha_{ind} \equiv$ property of the dopant and pH_2 in solid pH_2

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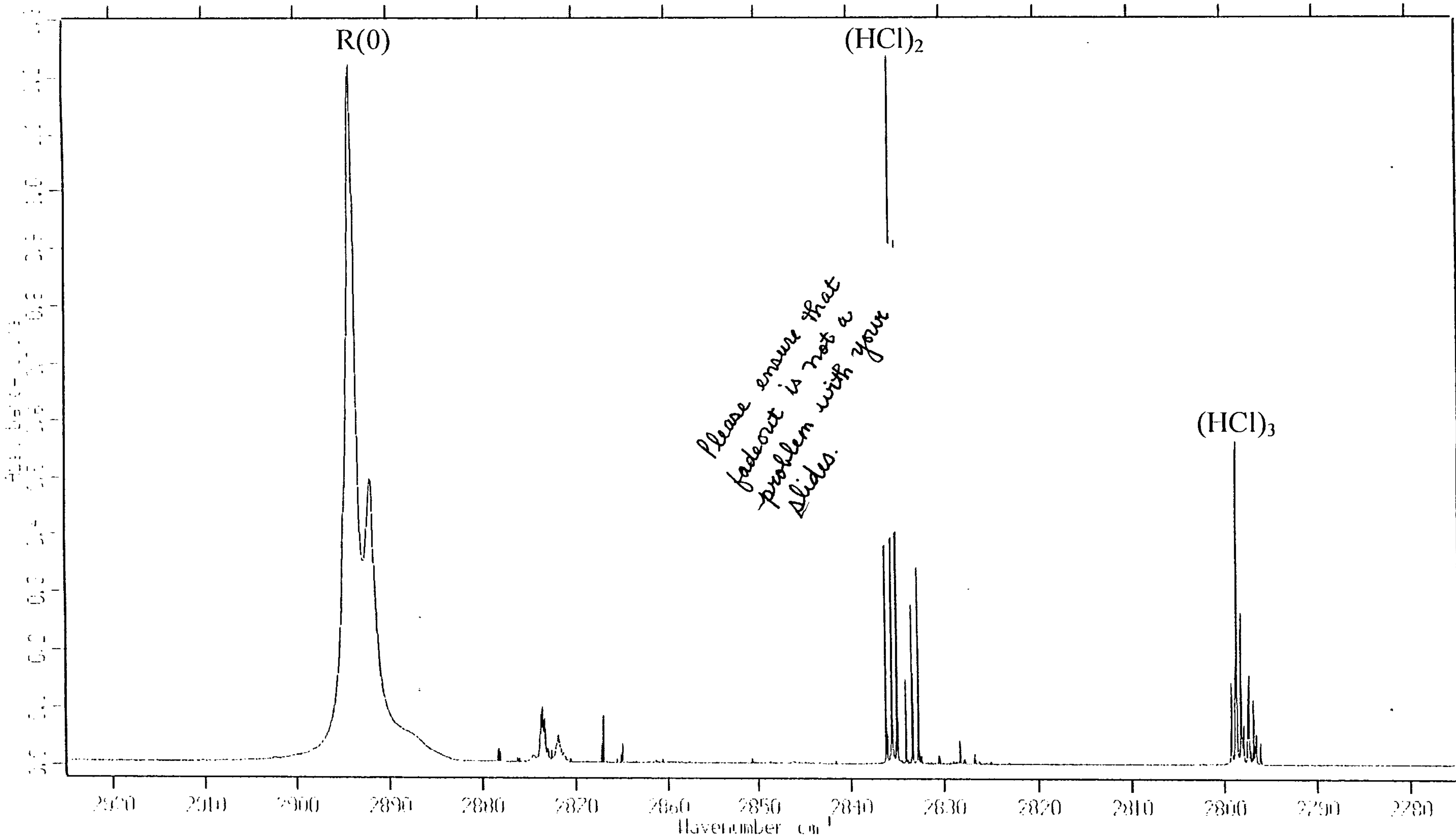
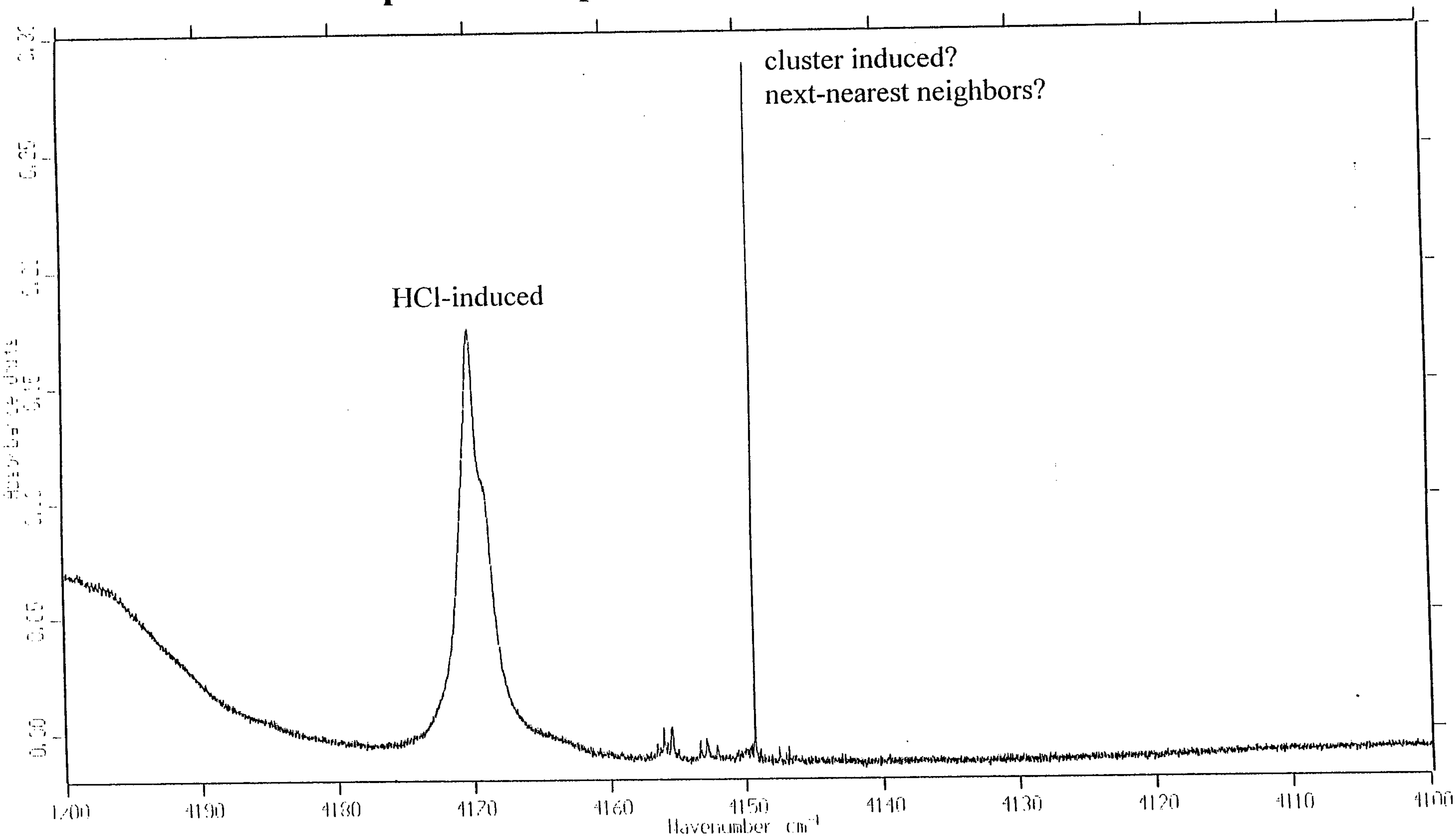
HCl/pH_2 at 2.4 K, 88 ppm, Resolution = 0.0075 cm^{-1}
Annealed Sample, HCl Absorptions Region



Please ensure that fadeout is not a problem with your slides.

OW: SUDS

HCl/pH_2 at 2.4 K, 494 ppm, Resolution = 0.0075 cm^{-1}
As Deposited Sample, Induced Absorption Region



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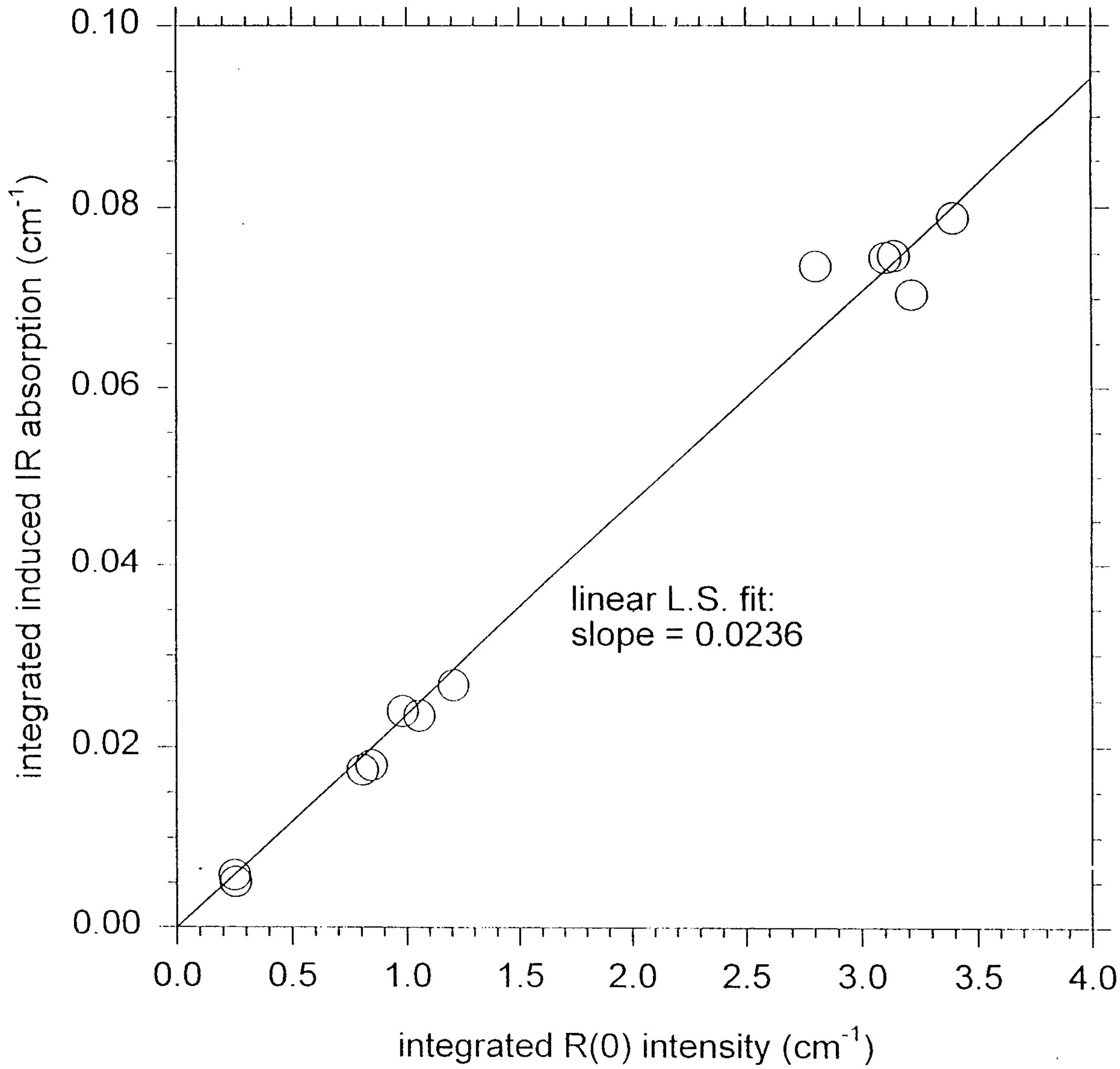
Correlation between HCl-Induced pH_2 IR Absorption and HCl R(0) Absorption



OM 5/2/06

HCl-Induced pH_2 Intrinsic IR Absorption Strength

$$\int \alpha_{ind}(HCl/pH_2)d\nu = 0.0236 \int \alpha(HCl)\, d\nu$$

literature: $\int \alpha(HCl)\, d\nu = 19.8$ km/mol*

$$\therefore \quad \int \alpha_{ind}(HCl/pH_2)\, d\nu = \underline{\mathbf{0.47\ km/mol}}$$

*K. N. Rao, ed., *Molecular Spectroscopy: Modern Research Vol. III* (Academic Press, Inc., New York, 1985).

Question: What is the maximum, measurable concentration of HCl/pH_2?

Assume: a) 1 mm thick sample

b) $\int A_{max}\, d\nu = 2\ cm^{-1}$

Answer:

$$c_{max} = \frac{2.303\ (2\ cm^{-1})}{(0.1\ cm)(4.7x10^4\ \frac{cm}{mol})}$$

$$= 9.9 \times 10^{-4}\ mol/cm^3$$

$$\Rightarrow 2.3\%\ HCl/pH_2$$

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SUMMARY

For millimeters thick, heavily-doped samples, direct absorption spectroscopy fails because of limitations on dynamic range and achievable signal-to-noise levels.

Dopant-induced pH_2 transitions are a possible solution to this problem.

1) appear to obey Beer's Law
2) are very weak IR transitions (i.e., increased dynamic range for heavily doped samples)

For HCl in pH_2, the intrinsic absorption strength of the induced transition is approximately 2.4% of the intrinsic absorption strength of HCl in the gas phase.

Can calculate the maximum measurable concentration for a HCl-doped pH_2 solid: 2.3% for a 1 mm thick sample, achieving objective of measuring ~1% concentration in millimeters thick samples.

FUTURE DIRECTIONS

We are in the process of completing a survey of various dopants in solid pH_2 to determine the generality of using the induced absorptions for concentration measurements.